

Maximum Entropy Closure for Flows in Transiently Driven Nonequilibrium Systems

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The question of deriving general force/flux relationships that apply out of the linear response regime is a central topic of theories for nonequilibrium statistical mechanics. This work traces models for force/flux relations from early through modern theories of stochastic thermodynamics to show that the *form* of response theories in driven, nonequilibrium transient dynamics and their symmetries are essentially solved problems. We find agreement between three different approaches: the projector-operator and fluctuation-dissipation theorem, the fluctuation theorem and chaotic hypothesis, and finally a simple maximum entropy approach combining ideas from Jaynes with large deviation theory. The points of agreement emphasize the importance of working with transition distributions. Our comparison is illustrated by extensive numerical simulations of the periodic Lorentz gas (Galton board) and α -Fermi-Pasta-Ulam chains, two paradigmatic problems in nonequilibrium statistical mechanics. Both are started from transient initial conditions and evolved under constant driving forces. We have phrased the comparison in such a way that it is actually simpler to work in nonlinear regimes without steady-states. Outstanding areas of debate between the approaches, related to existence and use of steady-states, how to define appropriate coarse-grained coordinates, and how to interpret the dissipation function, do not alter the main conclusion.

I. INTRODUCTION

The recent, repeated statements that there is no simple, unifying theory for nonequilibrium statistical mechanics call the question of how the many existing, rather complete, frameworks for attacking nonequilibrium problems are all related. Although there is a growing consensus[1–4] that theories describing the full force/flux curve are connected by simple, general principles, the proofs are usually too complex to make comparisons. This work quickly sketches the basic approaches to show that there is a canonical form for phrasing the statistics of nonequilibrium dynamics.

There are multiple theories of nonequilibrium statistical mechanics that have developed into essentially complete programs for studying stochastic molecular systems driven by external forces. Perhaps the earliest among these is thermodynamics itself, originally developed to describe the energy flows in engines driven by combinations of work and heat. The first and second laws are founded on the laws of conservation of energy, volume, mass, and charge, and therefore apply to all macroscopic nonequilibrium situations. Moreover, the equilibrium relations provide a default model for delivering these quantities from the laboratory into an arbitrary dynamical system in any state.[5] In the thermodynamic limit, the equilibrium theory of statistical mechanics predicts the general form for probabilities of conserved quantities from information about the environmental reservoirs.[6]

It is the goal of nonequilibrium statistical mechanics to provide the general form for rates of movement of conserved quantities within and between systems. Such equations of motion are the nonequilibrium analogues for the equilibrium equations of state. Also known as force/flux relationships, these equations of motion should give probabilities for the kinetics of processes given information about the state of the system and environment.

In the sections that follow, I describe two paradigmatic

examples of nonlinear, nonequilibrium systems and give a very brief catalogue of known results for each. Next, two major approaches for predicting the form of the force/flux relationships in these systems are sketched. From that review, it will become clear that there is essentially only one way to work consistently with transition distributions. This insight is incorporated into a third theory, where energy balances enter naturally into the expression for the transition probability.

Differences between the theories, discussed in the conclusion, warrant special attention for ill-behaved systems, where poor choices of coarse coordinates exist or where external forces can cause ‘blow-up’ of the dynamics. Despite these open topics, it can be concluded that, for typical systems, the statistical description of nonequilibrium kinetics in terms of forces and flows is a well-posed problem with many, complimentary methods of attack.

II. DYNAMICAL SYSTEMS INVESTIGATED

A. Periodic Lorentz Gas

The periodic Lorentz gas describes a system of fixed scattering centers that cause rigid-body collisions of a single, spherical gas particle. The deflections of the studied gas particle cause it to undergo a random walk, mimicking an ideal gas. This model has been applied to study electron conductivity.[7] The zero-forcing case where the scattering centers have a spatially periodic order was studied by Sinai,[8] who showed that the trajectory of the particle over long times converges to a Brownian random walk, and that the expected direction of motion remains constant over time. The evolution of the probability density can be shown to converge to a Boltzmann transport equation,[9, 10] and even has intuitive diffusive properties under a small, constant external force.[11] A review of approaches to the Lorentz gas was given by Spohn.[12]

In two dimensions, with a constant applied force, the periodic Lorentz gas is also known as the Galton board, which has an even longer history. Between scattering centers, the particle follows a parabolic trajectory, making exact analysis difficult. An analysis using a constant kinetic energy thermostat showed strong chaotic properties, including fractal scaling of the probability distributions for particle-scatterer impact.[13] With elastic collisions, the kinetic energy of the particle increases linearly as the particle falls. For this case, it has recently been shown that the particle velocity grows with time as $t^{1/3}$, and that (analogous to the Gambler's ruin problem) for large enough starting velocity the particle will return to its initial height with probability 1.[14]

To illustrate the full fluctuation theorems for this system, the following 2D simulation was carried out. A constant acceleration ($E\hat{x} - g\hat{z}$) is applied to a rigid disk in the presence of a fixed hexagonal close-packed lattice of scatterers. On each collision, the normal component of the particle's velocity is reversed, and a Langevin impulse is applied to its velocity. The thermostat is important to dissipate energy added by the constant external force. Because the object is macroscopic, the random impulses are negligible. To be consistent, the tangential velocity is subject to an independent impulsive Langevin scattering. This required tracking the particle's angular velocity.

Figure 1a shows four randomly chosen trajectories for the system, along with the complete histogram collected at row 10. The flux, J , is identical to the final bin number, determined from the x -coordinate. The results presented here were collected from the hexagonal lattice shown with scatterer radius $0.4L$, where L is the lattice spacing that fixes the dimension of length. The time scale, τ , was set so that the gravitation constant is $9.8m/s^2 = 1L/\tau^2$. 102,400 trajectories were simulated with uniform random starting locations on the line $y = 0, x \in (-0.1L, 0.1L)$ and velocities chosen from a Gaussian distribution with variance $(\beta M)^{-1} = 5.292 \cdot 10^{-19} \tau^2/L^2$. This is consistent with a physical scatterer diameter of 6.35 cm and mass of 5 g. Complete details are in the appendix.

B. Fermi-Pasta-Ulam Chains

To examine the time-course of energy redistribution between harmonic motions of a crystal lattice, Fermi, Pasta, and Ulam (FPU) simulated 32 points moving in 1D with unit masses and coordinates,[15] $x_j, j = 1, \dots, N$. This work uses periodic boundaries, so $x_0 = x_N$. The potential energy function is,

$$U(x) = \sum_{j=0}^{N-1} V(x_{j+1} - x_j) \quad (1)$$

$$V(r) = r^2/2 + \alpha r^3/3. \quad (2)$$

They discovered that for small anharmonic terms, energy did not seem to exchange, but only to oscillate reg-

ularly between harmonic modes. Recent, much longer, simulations and theory have shown that systems with small α do, in fact, equilibrate but on an enormously long time-scale on the order of α^{-8} . [16] This phenomenon has been explained as due to the nearness of $V(r)$ with the potential for the Toda lattice, $e^r - r - 1$, which is exactly integrable.

Fig. 1b shows example trajectories of energy flow from mode $k = 7$ to $k = 3$ in the FPU system at $\alpha = 0.1$. The energy for mode k was computed using the usual expression,

$$E_k = \frac{1}{2N}(|P_k|^2 + \omega_k^2|X_k|^2), \quad (3)$$

in terms of discrete Fourier modes,

$$\begin{aligned} X_k &= \sum_{j=1}^N u^{-jk} x_j, & u &\equiv e^{2\pi i/N} \\ P_k &= \sum_{j=1}^N u^{-jk} p_j, & \omega_k^2 &\equiv |u^k - 1|^2. \end{aligned} \quad (4)$$

To provide a steady-state with energy flow, both modes $k = \pm 3$ and $k = \pm 7$ were coupled to Langevin thermostats with $\beta_3 = 1 + \Delta\beta$ and $\beta_7 = 1 - \Delta\beta$, respectively, and $\sigma = 0.1$. The energy flux was computed by noting the identity for the total energy in each mode, $E_k(t) - E_k(0) = Q_k + Q_k^{\text{Langevin}}$. That is, the integrated heat flux, Q_k , was found by subtracting the cumulative energy added to mode k by the Langevin thermostat from total energy differences computed by Eq. 3. When $\alpha = 0$, the modes are uncoupled, and $Q_k = 0$ regardless of thermostatting.

Distributions of $Q = Q_3 - Q_7$ presented here were calculated at time 1638.4 from a Verlet integration scheme with timestep 0.01. They include an initial transient of approximately 100 time units because the initial conditions were chosen from the canonical distribution for the harmonic system ($\alpha = 0$) at uniform temperature $\beta = 1$.

Fig. 1c,d shows that the flow is a nonlinear function of the applied force (\vec{E} for the Lorentz gas or $\Delta\beta$ for the FPU lattice). This is especially apparent at large values of the forcing, where the probability distributions over flow (J for the Lorentz gas or Q for the FPU lattice) are markedly non-Gaussian. These flows are totals, integrated over the first 10 rows for the Lorentz system or the first 1638.4 time units of the FPU lattice. Because of this they include part of the initial transient as it relaxes to a conducting steady-state.

III. MAXIMUM TRANSITION ENTROPY

This section derives a canonical form for the transition probability distribution. Although this form can be used to derive the transient fluctuation theorems, it does not center on the operation of time-reversal. Instead, it

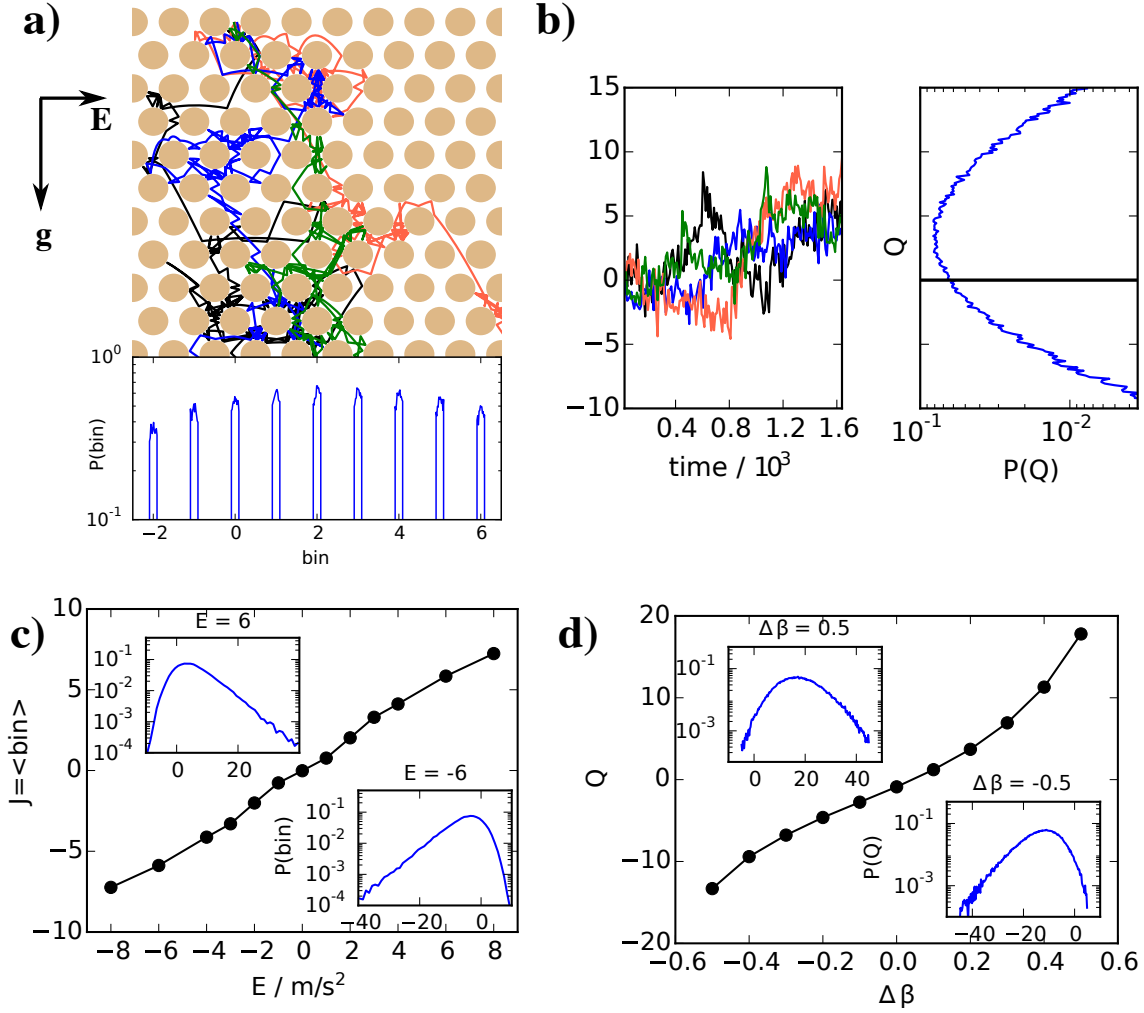


FIG. 1. Tracking the horizontal flow through the Galton board setup (left panels) or the heat flux from mode 7 to mode 3 in the Fermi-Pasta-Ulam lattice (right panels). Example trajectories, along with a histogram of total flux at a single applied force are shown in a,b, while c,d summarize all simulations by showing the average flux as a function of applied force. The insets of c,d show histograms of the flux at large values of the force.

relies on assuming that, over time, irreversibility drives the statistics toward a well-defined distribution of the average flux. It is called MaxTrans here, owing to this particular derivation,[17] however similar large deviation functions have been announced and studied by several authors.[4, 30] In what follows, the flows, J , relate to both J and Q in our numerical simulations.

The major result of this theory is that, under random-enough conditions, the force-flux relationship has a maximum entropy structure with the average flux, J becoming a function of a Lagrange multiplier, λ . The Lagrange multiplier is a generalized force. In the numerical examples here, λ is a nonlinear function of E or $\Delta\beta$. The end of the section presents numerical results confirming this structure.

Our proof is by converting a counting problem solved by Jaynes[35] into the language of large deviation processes.[36] Assume each trajectory segment begins at $i = 0$ with flux $J_0 = 0$. At each step, the system makes an independent choice of the increment, $J_{i+1} - J_i = g^{(i+1)}$, from a fixed set of possibilities, $\{g_1, \dots, g_m\}$, chosen with multiplicities, $\{f_1, \dots, f_m\}$. Now, compute the number of ways to arrive at step n with total flux $J_n = J$. It is not hard to see that the answer satisfies,

$$M(n, J) = \sum_{j=1}^m f_j M(n-1, J - g_j). \quad (5)$$

The elementary solutions have the form,

$$M(n, J) = \mathcal{Z}_{\text{kin}}^n(\lambda) e^{-\lambda J}, \quad \mathcal{Z}_{\text{kin}}(\lambda) \equiv \sum_{j=1}^m f_j e^{\lambda g_j}. \quad (6)$$

Here, λ is not a free parameter, but is instead the generalized force of response theory required to produce the flux, J . In the relations below, λ is understood to be a function of the average flux, $\langle g \rangle$.

The logarithm of the multiplicity, M , plays the role of the entropy here. It is a function of the average flux, $J/n \asymp \langle g \rangle$, where “ \asymp ” means asymptotic convergence with large time, t . Therefore, by either large deviation theory[36] or the standard relations of statistical mechanics, the Lagrange multiplier is the value of λ that minimizes,

$$\frac{1}{n} \log M(n, J) \asymp \inf_{\lambda} [\log \mathcal{Z}_{\text{kin}}(\lambda) - \lambda \langle g \rangle]. \quad (7)$$

We can use inference to construct a probability distribution over each increment, $P(g^{(n)} = g_j)$, given that the long-time expectation value is $\langle g \rangle$,

$$\begin{aligned} P\left(g^{(n)} = g_j \middle| \sum_{k=1}^n g^{(k)} = J\right) \\ = \frac{P\left(g_j, \sum_{k=1}^{n-1} g^{(k)} = J - g_j\right)}{P\left(\sum_{k=1}^n g^{(k)} = J\right)} \end{aligned} \quad (8)$$

$$= \frac{f_j M(n-1, J - g_j)}{M(n, J)} \asymp \frac{f_j e^{\lambda g_j}}{\mathcal{Z}_{\text{kin}}(\lambda)}. \quad (9)$$

This reasoning is local in time, and should be expected to hold even for transient processes observed over time-intervals with sufficient noise. It is a simple consequence of the random process determining each increment, g_j . Obviously, the challenge in rigorous proofs is to show appropriate independence of these increments. A few works have discussed this problem.[4]

When those conditions are met, the transient fluctuation relation, Eq. 26, can be derived from Eq. 7. Define two processes, a ‘+’ process initiated from x_0 and a ‘-’ process initiated from x_n . Both points are arbitrary. Let the multiplicities for the first process be $f_j = P(x_n|x_{n-1}) \dots P(x_1|x_0)$, and those for the second be $\tilde{f}_j = P(x_{n-1}|x_n) \dots P(x_0|x_1)$. Finally, define $g_j = \sigma_j^+ = \sum_{i=1}^n \log[P(x_i|x_{i-1})/P(x_{i-1}|x_i)] = -\sigma_j^-$. Now, note that $\mathcal{Z}_{\text{kin}}^+(-\lambda - 1) = \mathcal{Z}_{\text{kin}}^-(\lambda)$, so that

$$\frac{1}{n} \log M_-(n, -J) \asymp \inf_{\eta} [\log \mathcal{Z}_{\text{kin}}^-(\eta) + \eta \langle g \rangle] \quad (10)$$

$$= \inf_{\lambda} [\log \mathcal{Z}_{\text{kin}}^+(\lambda) - (\lambda + 1) \langle g \rangle]. \quad (11)$$

Subtracting this from Eq. 7 completes the proof.

Postulates like Eq. 9 have been hinted at before in connection with Onsager-Machlup theory[37], but their generality and use for deriving more traditional fluctuation theorems has not been widely appreciated. A similar theory of Jaynes, named maximum caliber (MaxCal),[23] applied maximum entropy to the set of all trajectories, and did not maintain causality.[5] This shortcoming has not caused major issues where the theory has been applied, [38–40] since maximum caliber and MaxTrans make the same predictions when there is time translation invariance. However, it should be noted that path counting gives non-causal weights to trajectories, whereas the transition probabilities are always causal.

Both Jaynes[41] and Haken[42, 43] investigated maximizing the entropy of the transition distribution as a restriction of MaxCal. However, those works chose different average value constraints than the more recent works.[5, 17] Rather than constraining fluxes, related to the movement of the system at a given time, they used general moment constraints on the position at the final time, making the connection to stochastic dynamics indirectly through the Fokker-Planck equation. Because of the difference in constraints, those approaches did not get a direct kinetic partition function, \mathcal{Z}_{kin} , displaying force-flux relationships and FDTs.

It is clear that Eq. 9 has the same, canonical, structure as equilibrium statistical mechanics. In particular, the forces and average fluxes are conjugate thermodynamic variables,

$$\langle J | \lambda, \Gamma \rangle = \frac{\partial \log \mathcal{Z}_{\text{kin}}(\lambda, \Gamma)}{\partial \lambda} \quad (12)$$

$$\langle \delta J^2 | \lambda, \Gamma \rangle = \frac{\partial^2 \log \mathcal{Z}_{\text{kin}}(\lambda, \Gamma)}{\partial \lambda^2} \quad (13)$$

These averages are conditional on the starting-point, Γ , by the dependence of $\{g_j\}, \{f_j\}$ on Γ . Ref. [30] indirectly

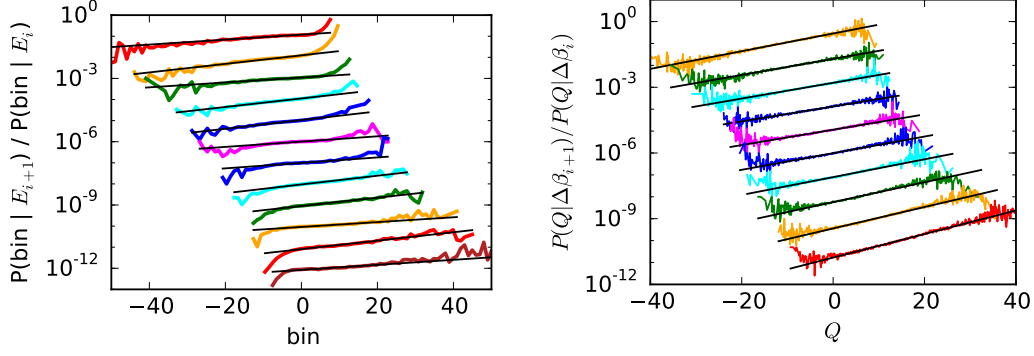


FIG. 2. Log-probability ratios for successive values of the applied force. Forces increase left-to-right, with each line shifted down by a factor of 10 for visual separation. Black lines show linear fits to these log-ratios. The left panel shows data from the Galton board, while the right shows heat conduction in the FPU lattice.

showed their use for deriving Onsager reciprocity. The full, causal, analogue of the Green-Kubo relations was demonstrated in Ref 17.

New relations between transition probabilities can be shown directly by subtracting Eq. 9 at two different applied forces,

$$\log \frac{P(J|\lambda')}{P(J|\lambda)} \asymp (\lambda' - \lambda)J - n \log \frac{Z_{\text{kin}}(\lambda')}{Z_{\text{kin}}(\lambda)} \quad (14)$$

Figure 2 illustrates this maximum entropy structure by plotting the ratios, $P(J|F')/P(J|F)$ for successive values of the applied force, $F = E$ or $\Delta\beta$. The probabilities were calculated from histograms of the final bin number (Galton board system) or total energy exchange (FPU lattice) using 120,400 independent trajectories for each value of the forcing. Despite the transient initial conditions, the very short simulation times, and the nonlinearity in the flux-force curves, the MaxTrans postulate, Eq. 14, appears to hold for both systems examined here.

The correspondence between λ and the applied force, (E or $\Delta\beta$) is not direct. Instead, in the same spirit as the Gibbs distribution, MaxTrans predicts a canonical form for transition probability distributions. The relationship between generalized forces, λ , and an applied physical force, is identifiable by any of three equivalent methods, *i*) checking the ratio of Eq. 14 for two different forces, *ii*) matching mean and variance of the flux to the expansion, $\langle J|\lambda' \rangle = \langle J|\lambda \rangle + (\lambda' - \lambda) \langle \delta J^2|\lambda \rangle + O(\Delta\lambda^2)$, *iii*) Green-Kubo style integration of the conjugate flux[5, 44], or *iv*) differentiating $d\sigma(\langle J \rangle)/d\langle J \rangle = \lambda$, where

$$\sigma(\langle J \rangle) = - \int dJ P(J|\lambda) \log P(J|\lambda). \quad (15)$$

Figure 3 compares methods *i* and *ii* by plotting $d\langle J|\lambda \rangle/d\lambda$ (lines) from the force-flux curves of Fig. 1 against the fluctuations $\langle \delta J^2 \rangle_\lambda$ (shown as points). The two smooth lines on each plot come from the derivatives obtained from 3rd and 7th order numerical differencing schemes. Differences between these lines are a measure of the uncertainty in collected force *vs.* flux data. The

correspondence, $\lambda = \lambda(E)$ or $\lambda(\Delta\beta)$, was made by the fits to the slopes in Fig. 2. Linear response predicts that $\langle J \rangle$ will be proportional to λ , λ proportional to the force, and hence $\langle \delta J^2 \rangle$ will be constant. While this almost holds near the origin, our numerical data show the validity of Eq. 14 well out of the linear response regime.

Finally, energy balances can be used to construct a canonical form for the transition probability by maximizing the entropy of the probability for deviations from the principle of stationary action, $\delta\mathcal{A}[x]/\delta x = F - \dot{p}$, given known average changes in the conserved quantities,[5]

$$D = \left\langle \left| \frac{\delta\mathcal{A}[x]}{\delta x} \right|^2 dt \right\rangle, dE = - \left\langle dx \cdot \frac{\delta\mathcal{A}[x]}{\delta x} \right\rangle, \\ d\Theta = - \left\langle dt \cdot \frac{\delta\mathcal{A}[Rx + t]}{\delta R, t} \right\rangle, \dots \quad (16)$$

This canonical form *derives* the Langevin equation, as can be shown from factoring the quadratic in

$$P(F - \dot{p}|x, p) \propto e^{-\langle \left| \frac{\delta\mathcal{A}[x]}{\delta x} \right|^2 dt \rangle / 2\sigma^2 + \beta \langle dx \cdot \frac{\delta\mathcal{A}[x]}{\delta x} \rangle / 2}. \quad (17)$$

The Lagrange multiplier for D is defined to be $1/(2\sigma^2)$. The multiplier for the energy flux turns out to be half the inverse temperature, $\beta/2$, regardless of the others. The multipliers for the last quantity are net external forces related to the pressure and momentum. The notation $\delta/\delta R, t$ describes the set of derivatives with respect to the 3 components of the translation, t , and the 6 independent components of the 3×3 rotation/scale matrix, R .

The canonical form codifies flux/force relations in a coordinate-independent way using a maximum entropy structure. Because of this, it provides facile derivations for both time-dependent Green-Kubo response theories and the fluctuation theorems when the postulate of Eq. 9 holds. Its shortcoming is that it does not directly predict the relationship between the forces and flows, e.g. β and $\langle dE \rangle$. This, however, is exactly the well-known problem of determining the equations of state in equilibrium statistical mechanics.

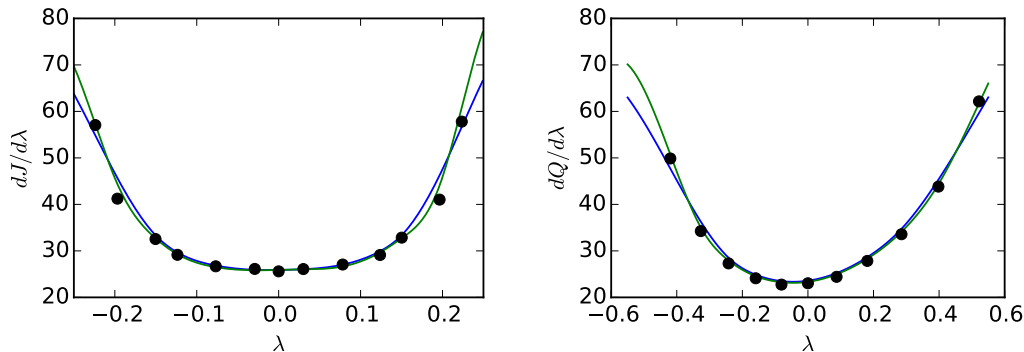


FIG. 3. Comparison between asymptotically equivalent expressions for the conductivity coefficient. The lines show different numerical estimates of derivatives of the flux vs. force curves ($d\langle J \rangle / d\lambda$) computed from alternate finite difference methods, while the variance of the flux ($\langle \delta J^2 | \lambda \rangle$) is shown as individual points. The blue line uses a 3rd order finite difference interpolation of $J(\lambda)$ (Fig. 1c,d) and the green line uses a 7th order interpolation from the same data. The left panel shows data from the Galton board, while the right shows heat conduction in the FPU lattice.

IV. DISCUSSION AND COMPARISON

This section provides further background and highlights the connections between theories by presenting short derivations of alternative approaches to the present problem. Often, applied literature provides specialized fluctuation-dissipation or fluctuation theorems that give little hint as to how they may be generalized or extended. In fact, the original derivations allow quite a bit of flexibility in defining what forces and flows can enter, and can be put into a form very much resembling our major results (Eqns. 12, 13, and 14). We discuss these alternative viewpoints by standardizing the notation and re-stating the theorems in terms of time-derivatives (flows) rather than absolute positions.

A. Projector-Operator and Fluctuation-Dissipation Theorems

The projector-operator theory gives a rigorous, general equation of motion for the probability distribution of coarse coordinates like the particle position or the energy in each mode. The theory clearly indicates where closure relations are required. This section shows how the simplest closure relations with Gaussian noise can be derived by analogy to Gaussian processes. The result provides time-dependent Green-Kubo relations applicable at nonzero driving force. They are linear because they predict the slope of the flow *vs.* force curve.[17]

An accessible derivation of the projector-operator theory was given by Nordholm and Zwanzig[18] with the

result,

$$\begin{aligned} \frac{\partial}{\partial t} \mathbb{P}f(t, \Gamma) &= -\mathbb{P}i\mathcal{L}\mathbb{P}f(t, \Gamma) \\ &+ \int_0^t ds \mathbb{P}i\mathcal{L}e^{-is(1-\mathbb{P})\mathcal{L}}(1-\mathbb{P})i\mathcal{L}\mathbb{P}f(t-s, \Gamma) \\ &- \mathbb{P}i\mathcal{L}e^{-it(1-\mathbb{P})\mathcal{L}}(1-\mathbb{P})f(0, \Gamma). \end{aligned} \quad (18)$$

The operator, \mathbb{P} , projects the phase-space probability density, $f(t, \Gamma)$ onto a subspace of the full phase space, $\Omega = \{\Gamma\}$. The Liouville operator is defined in terms of the Poisson brackets, $i\mathcal{L}J = \{J, H\} = g/dt$. There is no difficulty interpreting this subspace as an arbitrary manifold lying inside Ω . For any point, Γ , we can define the projected point on the manifold as $\phi(\Gamma)$ so that

$$\mathbb{P}f(\Gamma) = \int_{\Omega} d\Gamma' \delta(\Gamma - \phi(\Gamma'))f(\Gamma'). \quad (19)$$

The projected equation of motion (Eq. 18) implicitly defines the probability distribution of transition events, $g = \phi(\Gamma) \rightarrow \phi(\Gamma')$. It is trivial to re-cast it in this way, since $dt \frac{\partial}{\partial t} \mathbb{P}f(t, \Gamma) = \int dg \mathbb{P}(\Gamma|\Gamma', dt) f(t', \Gamma') - f(t', \Gamma)$ as the timestep, $dt \rightarrow 0$.

The push-forward operation, $i\mathcal{L}\mathbb{P}f(t, \Gamma)$, in both of the first two terms refers explicitly to this transition. The three parts of the equation of motion on the manifold (Eq. 18) have the interpretation of *i*) the deterministic transition ($\mathbb{P}i\mathcal{L}\mathbb{P}$) for points on the manifold, *ii*) the memory function describing the predictable, but delayed effect due to earlier transitions, $(1-\mathbb{P})i\mathcal{L}\mathbb{P}f(t-s, \Gamma)$, and *iii*) the ‘random’ noise part due to initial conditions not on the manifold.

Because they are off the manifold, the equation of motion makes it clear that closure relations are required for describing parts *ii*) and *iii*). Specific choices for those closures form the starting points for mode coupling theory[18] and nonlinear fluctuating hydrodynamics.[19] That theory has also been applied to dynamics in large-FPU chains.[20]

In practice, most applications of the theory have used linear closure relations, which give rise to linear transport equations.[21] Nonlinear closures are most easily understood by comparison to the linear theory.[22] It has been pointed out[23] that the principle results of the linear theory are identical to linear regression.

The linear regression case has been treated in a very general way in the Gaussian process literature. The critical assumptions are that the random noise obeys Gaussian statistics and that the coefficients of the memory function depend only on time, not on the process history. The equations below relate to the two systems considered here by replacing g with the horizontal motion of the disk, dJ , or the heat transfer, dQ , over a small amount of time. The regression equations can be summarized by the assumption,[24]

$$P(\{g(t_i)\}_0^n) = GP[m(t_i), k(t_i, t_j)] \quad (20)$$

which implies the following generating process,

$$g(t_n) = m(t_n) + \sum_{j,k=1}^n k(t_n, t_{n-j}) k_{n-j;n-k}^{-1} \times (g(t_{n-k}) - m(t_{n-k})) + \sigma_n Z_n \quad (21)$$

$$\sigma_n^2 = k(t_n, t_n) - \sum_{j,k=1}^n k(t_n, t_{n-j}) k_{n-j;n-k}^{-1} k(t_n, t_{n-k}) \quad (22)$$

Here, GP denotes a Gaussian process, which is a multivariate normal distribution with mean $m(t)$ and variance-covariance matrix $k(t, t')$. Eq. 21 states the applicable fluctuation-dissipation theorem – namely that the probability of g at the next step has a Gaussian distribution with a mean that is linear in the random increments, $g(t_k) - m(t_k)$, and a variance, σ_n^2 , that is reduced by knowledge of the process history. The variable Z_n is an independent sample from the standard normal distribution.

This closure is demonstrated by noting the terms in Eq. 21 correspond 1:1 with those of Eq. 18. Brownian motion theory is recovered when g is taken to be the momentum. Then $m(t)$ is the drift velocity and $k(t, t) = k_B T/m$ near equilibrium. Its time-derivative describes Langevin dynamics, where g_n is the momentum update, $p_n - p_{n-1}$.

From these identifications, a little algebra shows that applying an external force to shift $g_0 \rightarrow g_0 + F_0^{\text{ext}}$ will accumulate a net effect at step k of,

$$\delta g_{k \leftarrow 0} = [k(t_k, t_I)]^T k_{IJ}^{-1} \begin{bmatrix} \delta g_0 \\ \delta g_{1 \leftarrow 0} \\ \vdots \\ g_{k-1 \leftarrow 0} \end{bmatrix} \quad (23)$$

The recursion is solved by

$$\delta g_{k \leftarrow 0} = \frac{k(t_k, t_0)}{k(t_0, t_0)} F_0^{\text{ext}}. \quad (24)$$

This externally forced process could have been derived extremely easily by adding an exponential bias to the basic Gaussian process (Eq. 20),

$$P(\bar{g}|F^{\text{ext}}) \propto e^{-(\bar{g}-\bar{m})^T k^{-1}(\bar{g}-\bar{m})/2 + (\bar{g}-\bar{m})^T (F^{\text{ext}}/\text{diag}(k))}. \quad (25)$$

This is the revised Onsager-Machlup action functional approach.[25, 26]

The linear transport theory can be re-derived in a simplified way as a Gaussian process. The technical content of the celebrated fluctuation-dissipation theorem in this case is a statement of how dissipation of an external force, $\sum_{j < n} k(t_n, t_{n-j})$, is related to fluctuations of the current, $k(t_i, t_j) = \langle \delta g_i \delta g_j \rangle$.

We can see that this line of attack applies to time-dependent processes, but it is not yet clear how to make the theory properly nonlinear. The major idea of Sec. III is to replace the fitting ansatz of Eq. 20 with a single-step fitting ansatz at time i , where m_i and k_{ij} are arbitrary nonlinear functions of the history, $\{g\}_0^{i-1}$.

B. Fluctuation Theorems and Chaotic Hypothesis

Fluctuation theorems address the probabilities of transitions even more directly. Specifically, they transform symmetries of the dynamical equations into symmetries of integrated quantities such as work and heat. They have a history stretching back to Callen and Welton,[27] who proved a fluctuation theorem showing the odds of heat, Q , flowing from cold to hot vs. the reverse process was proportional to $\exp(Q\Delta\beta)$.

Since the literature on fluctuation theorems is large, I provide here only a few results. The first fluctuation theorems about atomistic trajectories were developed by several groups,[28, 29] who proved theorems of the form,

$$\frac{1}{t} \log \frac{P(g = \sigma(t, \Gamma)/t | x_0 \rightarrow x_n)}{P(g = -\sigma(t, \Gamma)/t | x_n \rightarrow x_0)} \asymp g \quad (26)$$

The conditions, x_0 or x_n , indicate whether the trajectory is initiated from a starting or ending point. For the transient fluctuation theorem, the microscopic entropy production is identified with the time-integral over a trajectory of length t starting from $\Gamma(0) = \Gamma$,

$$\sigma(t, \Gamma) = \int_0^t dt D(\Gamma(t)), \quad (27)$$

where $D(\Gamma)$ is the ratio of phase space volume between the last and next time-step, $|i\mathcal{L}(d\Gamma)|/|d\Gamma|$. Because of the dependence on the starting/ending point, there are differences in the relations and proofs depending on whether the starting states are fixed or chosen at random from an SRB measure (steady-state), whose existence and uniqueness requires additional assumptions.[30]

In the case where a dynamical system can be modeled as a finite-state Markov process, a new version of the

fluctuation theorem (Eq. 26) can be shown,[31, 32] where σ (W of Ref. 31) is the log-ratio of forward to reverse transition probabilities over $t = n$ steps of the Markov process,

$$\sigma(n, \Gamma) = \sum_{i=0}^{n-1} \log \frac{P(\Gamma_{i+1}|\Gamma_i)}{P(\Gamma_i|\Gamma_{i+1})}. \quad (28)$$

Although they apply in different cases, the two fluctuation relations essentially express the same measure of irreversibility, since the probability of a transition scales inversely with the starting volume, $P(\Gamma_{i+1}|\Gamma_i) \propto 1/|d\Gamma_i|$. [33]

Since the log-ratio of transition probabilities are often related to work and entropy production, the fluctuation theorems can make quantitative statements about energy exchange during transitions of a dynamic system. Although Eq. 26 appears to be a special case of Eq. 14, Eq. 26 has been proven to hold under more general conditions. Its relation to symmetry provides it with a unique perspective in that it is closer to a dynamical law than a statistical one.

It is also possible to specialize σ for describing transition probabilities of other coarse variables.[28, 34] This interpretation often refers to σ as a dissipation function, or, in reference to the Onsager-Machlup theory, as an action function. Our alternative derivation of σ as a generalized entropy in section III provides a simple explanation of this connection between σ and force/flux relations.

V. CONCLUSIONS

We have constructed a probability distribution over values of flows that occur during transitions using the tools of maximum entropy and Bayesian inference. It was shown that the nonlinear, maximum entropy structure is a general consequence of repeated random events. This is especially true as the number of transitions grows and holds for transient, driven processes. The success of the linear response methods and of the fluctuation theorems both rest on exploiting the existence of this structure within the transition distribution. Numerical simulations supported this conclusion – even for the challenging case of thermalization in the FPU lattice.

This theory has been directly related to two complementary methods of attack. The Green-Kubo relations provide quick estimates for the conductivities, even in transient steady-states. This work showed the connection by focusing on the transition quantities in Eq. 21, which have the same structure as Eq. 12 and 13. Fluctuation theorems provide connections with distributions of work and notions of irreversibility. We have shown the forward fluctuation theorem of Eq. 14 derives Eq. 26 when the flux is related to number of transitions. Transition distributions provide an entry point to these theories free from considerations of the local, thermostatic entropy (which is only well-defined in certain, special cases).[23, 25, 45, 46] All these approaches are structural in the sense that finding analytical expressions for long-time force/flux relationships is a difficult task, even for the Galton board[7, 11] and FPU heat models.[16, 47, 48] Nevertheless, the general structure shows that these relationships are directly analogous to equilibrium equations of state.

With any of these methods, it is possible that the dynamics exhibits very long correlation times, essential nonlinearities, or ill-behaved stationary states. Comparing theories, we can see that these conditions are related to a breakdown of the assumption that the external environment acts via a series of independent, random, impulses. The viewpoint of the exact dynamical school might be that either the dynamics is not hyperbolic, or $\sigma(\Gamma)$ is still correct, but requires a much longer memory to be well-approximated. The viewpoint of the projector-operator theory would be that the linear approximation breaks down, and a better choice of variables is needed. The viewpoint of maximum transition entropy would be that the dynamics is being predicted incorrectly because the prediction was based on incomplete information about the coarse-scale system.

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Appendix A: Lorentz Scattering Simulation

Collisions events were detected by solving the quartic equation to find intersections of parabolic trajectories with circular scatterers. By monitoring collisions with the unit cell boundaries, only one circle at each update step required testing.

At each scatterer collision time, the particle's normal velocity was reflected, and impulsive friction and random noise were added according to,

$$dp_n = -\lambda_n \sigma^2 v_n dt + \sigma d\mathcal{W}_n \quad (\text{A1})$$

$$dp_t = -\lambda_t \sigma^2 v_t dt + \sigma d\mathcal{W}_t. \quad (\text{A2})$$

Here, dp_n, dp_t represent the normal and tangential impulses added to the particle at the point of contact. To reach the impulsive force limit, we set $\lambda \sigma^2 dt/M \equiv \gamma$, so that $\frac{\sigma}{M} d\mathcal{W} = R\sqrt{\gamma/M\lambda}$, with R a sample from the standard normal distribution. This work used $\gamma = 0.01$ and solved λ to reproduce the canonical distribution at scaled inverse temperature, βM , from the main text.

The updated normal and tangential velocities (v') are therefore,

$$-v'_n = (1 - \gamma)v_n + \sqrt{2\gamma/(\beta M)} R_n \quad (\text{A3})$$

$$v'_t - v_t = -\gamma(v_t + r\omega) + \sqrt{2\gamma/(\beta M)} R_t \quad (\text{A4})$$

$$= r(\omega' - \omega)/2 \quad (\text{A5})$$

the final equation also states the update to the particle's angular velocity, ω , from the impulse. The particle's radius, r , can be absorbed into the units of the angular velocity because the moment of inertia of the disk is $Mr^2/2$. The identifications, $\lambda_n = \lambda_t = \beta/2$, come from equating the steady-state of repeated (isotropic, memoryless) collisions with a Boltzmann distribution,

$$P(v_n, v_t, r\omega) \propto e^{-\frac{\beta M}{2}((r\omega)^2/2 + v_n^2 + v_t^2)}, \quad (\text{A6})$$

in the limit where $\gamma \ll 1$. The proof of the steady-state is most easily done by using standard Gaussian formulas for the moment generating functions of v'_n or the pair $[v'_t, r\omega'/2]^T$.

Although highly unlikely because of the extremely large value of βM used here, it is technically possible that the random increment to v_n causes v'_n to remain inward. In these cases, no update was performed until a random number was found that left v'_n pointing outward. This is equivalent to choosing R_n from a truncated Gaussian distribution. Random noise is required by the fluctuation-dissipation theorem. With friction but no random noise, there were a few trajectories that settled into a stable limit, bouncing between only two scatterers. The angular momentum did not play a role in these limits, since it went quickly to zero.

Appendix B: FPU Simulation

Symplectic, volume-preserving dynamical integration schemes can be derived in a general way beginning from

a Lagrangian,[49]

$$L(x, \dot{x}) = \sum_i \frac{m_i \dot{x}_i^2}{2} - V(x). \quad (\text{B1})$$

Make the substitutions, $\dot{x} \rightarrow (x^{(t)} - x^{(t-1)})/\Delta t$, $x \rightarrow x^{(t)}$, to construct a discrete action functional,

$$A[\{x\}] = \sum_{t=1}^T L_d(x^{(t)}, x^{(t-1)}) \quad (\text{B2})$$

$$L_d(x', x) = \sum_i \frac{m_i (x'_i - x_i)^2}{2\Delta t} - \Delta t V(x'). \quad (\text{B3})$$

Requiring stationary action yields,

$$\frac{\partial L_d(x', x)}{\partial x'} + \frac{\partial L_d(x'', x')}{\partial x'} = 0, \quad (\text{B4})$$

which translates to the Strömer-Verlet scheme,

$$\frac{m_i}{\Delta t}(x'' - x') + \frac{m_i}{\Delta t}(x - x') + \Delta t \frac{\partial V(x')}{\partial x'} = 0. \quad (\text{B5})$$

Energy exchange processes can be monitored by examining various decompositions of the conserved quantity,

$$\frac{dE}{dt} = \frac{dx}{dt} \left(\frac{dp}{dt} - F \right). \quad (\text{B6})$$

Treating the cubic term as the source of an external force in the FPU system, the total forces can be decomposed to $F_{\text{int}} + F_{\text{cubic}} + F_{\text{lang}}$. This yields,

$$\frac{dE}{dt} = \frac{dx}{dt} \left(\frac{dp}{dt} - F_{\text{int}} \right) - \frac{dx}{dt} F_{\text{cubic}} = \frac{dx}{dt} F_{\text{lang}}. \quad (\text{B7})$$

Of course, the first term on the right side just integrates to the energy of the unperturbed harmonic system, $E_k(t) - E_k(0)$, explained in the main text. The 'heat flux' counts contributions from the second term – effectively thinking about $\frac{dx}{dt} F_{\text{cubic}}$ as coming from interaction with an external system. From this point of view, the time-derivative of the energy in each mode represents the flux of energy from both the anharmonic system and the Langevin thermostat.

The thermostatted equations of motion for FPU chains were derived by transforming coordinates to Fourier space using the discrete Lagrangian,

$$L_d(q', q) = \Delta t \sum_{j=0}^{N-1} \left[\frac{(q'_j - q_j)^2}{2\Delta t^2} - (q'_{j+1} - q'_j)^2/2 \right] - \Delta t V_c(q') \quad (\text{B8})$$

$$= \frac{\Delta t}{N} \sum_{k=0}^{N-1} \left[\frac{|Q'_k - Q_k|^2}{2\Delta t^2} - \frac{\omega_k^2}{2} |Q'_k|^2 \right] - \Delta t V_c(q'). \quad (\text{B9})$$

Here, V_c represents the cubic potential terms. According to MaxTrans, the exponent of the transition probability should be,

$$-\frac{\Delta t}{2\sigma^2} \left| \frac{\delta A[Q(t)]}{\delta Q(t)} \right|^2 + \frac{\beta}{2} dQ(t) \frac{\delta A[Q(t)]}{\delta Q(t)}. \quad (\text{B10})$$

Note how changing coordinate systems in this form amounts to transforming the deviations, σ , via the Jacobian dq/dQ . The thermostatted equations of motion for Q_k can be read off from the mean and variance found

by factoring Eq. B10

$$-\left(\frac{\delta A[Q_k(t)]}{\delta Q_k(t)} \right)^* \Delta t = -\frac{\beta_k \sigma_k^2}{2} dQ_k(t) + \sigma_k d\mathcal{W}_k. \quad (\text{B11})$$

This equation of motion must be interpreted as applying to only N degrees of freedom. Since $Q_k = Q_{-k}^*$, the unique discrete Fourier variables are $\text{Re}[Q_0, Q_1, \dots, Q_{\lceil (N-1)/2 \rceil}]$ and $\text{Im}[Q_1, \dots, Q_{\lfloor (N-1)/2 \rfloor}]$. The complex Wiener process $d\mathcal{W}_k$ requires $d\mathcal{W}_{-k} = d\mathcal{W}_k^*$, and should therefore have variance $\langle |d\mathcal{W}_k|^2 \rangle = dt$.